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(54) NON-AQUEOUS SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve the productivity and the shelf life by forming a positive electrode of two or more layers, of which the content of the positive electrode material in the mix is different from each other, and including insulating solid grains in the mix of a layer farthest from a collector.

SOLUTION: A positive electrode of this battery is formed by coating a collector with two or more layers including the positive electrode material, which can reversibly absorb and discharge lithium. These coating layer is respectively formed of the positive electrode material, binder and the conductive material. Especially, a layer farthest from the collector includes the insulating solid grains, but content of the positive electrode material in the mix of this layer is desirably set at 10% by weight or more and 60% by weight or less, and content thereof of other layer is set at 70% or more and 98% or less at an average. As the insulating solid grains, oxide is used, and titanium dioxide is most desirable.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] An internal short circuit is prevented and this invention relates to high capacity with good manufacture stability, and a high-voltage nonaqueous rechargeable battery.

[0002]

[Description of the Prior Art] Since the nonaqueous rechargeable battery using a lithium can desire the high voltage and high capacity, extensive development has been made. Usually these lithium secondary batteries consist of the positive electrode which contains reversibly the material in which occlusion emission is possible for a lithium and a negative electrode, nonaqueous electrolyte containing lithium salt, and a separator. However, these nonaqueous rechargeable batteries had the problem to which a positive electrode and a negative electrode short-circuit in each stroke under manufacture, and capacity falls. Moreover, when saved especially at an elevated temperature, the short circuit occurred and there was a problem that an early capacity was not recovered even if capacity falls and carries out a recharge during conservation of a cell.

[0003]

[Problem(s) to be Solved by the Invention] The technical problem of this invention is raising the productivity and the shelf-life property with the high voltage and high capacity of a nonaqueous rechargeable battery.

[0004]

[Means for Solving the Problem] A negative electrode which comes to paint a binder layer which contains reversibly a negative-electrode material in which occlusion emission is possible for a lithium on a positive electrode with which a technical problem of this invention comes to paint a binder layer which contains reversibly a positive-electrode material in which occlusion emission is possible for a lithium on a charge collector, and a charge collector, nonaqueous electrolyte containing lithium salt, and a nonaqueous rechargeable battery which consists of a separator -- setting -- this positive electrode -- a mixture -- from a layer more than two-layer [from which a content of an inner positive-electrode material differs] -- becoming -- a mixture of furthest layer from a charge collector -- it was attained by nonaqueous rechargeable battery characterized by containing an insulating solid particulate in inside.

[0005]

[Embodiment of the Invention] Although the desirable mode of this invention is explained below, this invention is not limited to these.

(1) The negative electrode which comes to paint the binder layer which contains reversibly the negative-electrode material in which occlusion emission is possible for a lithium on the positive electrode which comes to paint the binder layer which contains reversibly the positive-electrode material in which occlusion emission is possible for a lithium on a charge collector, and a charge collector, the nonaqueous electrolyte containing lithium salt, and the nonaqueous rechargeable battery which consists of a separator -- setting -- this positive electrode -- a mixture -- from the layer more than two-layer [from which the content of an inner positive-electrode material differs] -- becoming -- the mixture of the furthest layer from a charge collector -- the nonaqueous rechargeable battery characterized by containing an insulating solid particulate in inside.

(2) this positive-electrode layer -- from the layer more than two-layer -- becoming -- the mixture of the furthest layer from a charge collector -- a nonaqueous rechargeable battery given in the term 1 characterized by for the contents of an inner positive-electrode material being 10 % of the weight or more and 60 % of the weight or less, and the contents of the positive-electrode material of other layers being 70 % of the weight or more and 98 % of the weight or less on an average.

(3) A nonaqueous rechargeable battery given in the terms 1 or 2 characterized by the insulating solid particulate contained in the furthest layer from the charge collector of this positive electrode being an oxide.

(4) A nonaqueous rechargeable battery given in any 1 term of the terms 1-3 characterized by this insulating solid particulate being a titanium dioxide.

(5) this negative-electrode material -- mainly -- an amorphous chalcogen compound -- and -- or a nonaqueous rechargeable battery given in any 1 term of the terms 1-4 characterized by consisting of an amorphous oxide.

(6) this negative-electrode material contains three or more sorts of atoms chosen mainly from periodic tables 13, 14, and 15 and 2 group atom -- mainly -- an amorphous chalcogen compound -- and -- or a nonaqueous rechargeable battery given in the term 5 characterized by consisting of an amorphous oxide.

(7) A nonaqueous rechargeable battery given in the term 6 to which a kind is characterized by the thing of this negative-electrode material shown by the general formula (1) at least.

$M1M2pM4qM6r$ General formula (1)

(M1 and M2 are chosen from Si, germanium, Sn, Pb, P, B, aluminum, and Sb in difference among a formula -- a kind and M4 [at least] are chosen from Mg, calcium, Sr, and Ba -- a kind and M6 [at least] are chosen from O, S, and Te -- in a kind, and p and q, Each 0.001-10r expresses the numeric character of 1.00-50 at least.)

(8) A nonaqueous rechargeable battery given in the term 7 to which a kind is characterized by the thing of this negative-electrode material shown by the general formula (2) at least.

$SnM3pM5qM7r$ General formula (2)

M3 is chosen from Si, germanium, Pb, P, B, and aluminum among a formula -- a kind and M5 [at least] are chosen from Mg, calcium, Sr,

and Ba -- a kind and M7 [at least] are chosen from O and S -- in a kind, and p and q, Each 0.001-10r expresses the numeric character of 1.00-50 at least.

At least one sort of this positive-electrode material (9) Li_xCoO_2 , Li_xNiO_2 and Li_xMnO_2 , $\text{Li}_x\text{CoNi}_{1-a}\text{O}_2$, $\text{Li}_x\text{CoV}_{1-b}\text{O}_2$, $\text{Li}_x\text{CoFe}_{1-b}\text{O}_2$, $\text{Li}_x\text{Mn}_2\text{O}_4$, and $\text{Li}_x\text{MnCo}_2\text{-cO}_4$, $\text{Li}_x\text{MnNi}_2\text{-cO}_4$, $\text{Li}_x\text{MnV}_2\text{-cO}_4$, $\text{Li}_x\text{MnFe}_2\text{-cO}_4$ (among a formula) $x=0.02-1.2$, $a=0.1$ to 0.9 , $b=0.8$ to 0.98 , $c=1.6-1.96$, a nonaqueous rechargeable battery given in any 1 term of the terms 1-7 characterized by being $z=2.01$ to 2.3 .

(10) A nonaqueous rechargeable battery given in any 1 term of claims 1-9 characterized by applying the water distribution object with which a negative-electrode sheet contains a negative-electrode material, a binder, and an electric conduction agent on copper foil.

(11) A nonaqueous rechargeable battery given in any 1 term of claims 1-10 characterized by connecting a lithium metal to a negative-electrode sheet electrically, and inserting a lithium ion in a negative-electrode material beforehand according to the electrochemical reaction in a cell.

[0006] This invention is explained in full detail below. The negative electrode which comes to paint the binder layer which contains reversibly the negative-electrode material in which occlusion emission is possible for a lithium on the positive electrode with which this invention persons come to paint the binder layer which contains reversibly the positive-electrode material in which occlusion emission is possible for a lithium on a charge collector, and a charge collector. The cause that the manufacture yield of the nonaqueous electrolyte containing lithium salt and the nonaqueous rechargeable battery which consists of a separator is bad, As a result of considering wholeheartedly the cause that capacity falls at the time of conservation, this positive electrode and/or this negative electrode, respectively A positive-electrode material, from the layer more than two-layer [containing a negative-electrode material] -- becoming -- the mixture of the positive-electrode material of each class, or a negative-electrode material -- amelioration of a manufacture yield and shelf life can be performed by changing an inner content -- the mixture of the especially furthest layer from the charge collector of this positive electrode -- it traced to inside that amelioration of a manufacture yield and shelf life could be further performed by containing an insulating solid particulate, and it was reached at this invention. Here, the negative electrode used by this invention comes reversibly to paint a lithium the negative-electrode material in which occlusion emission is possible on a charge collector. There may be a protective layer in the upper layer of this negative-electrode binder layer. As for this protective layer, it is desirable to consist of a solid particulate and water-soluble polymer.

[0007] the desirable negative-electrode material of this invention -- mainly -- an amorphous chalcogen compound -- and -- or it is an amorphous oxide. moreover, a desirable negative-electrode material contains three or more sorts of atoms chosen mainly from periodic tables 13, 14, and 15 and 2 group atom -- mainly -- an amorphous chalcogen compound -- and -- or it is an amorphous oxide.

[0008] As for the negative-electrode material used by this invention, it is desirable that it is mainly amorphous at the time of cell inclusion. An amorphous substance is an object which has the broadcloth dispersion band which has top-most vertices from 20 degrees to 40 degrees with 2theta value with the X-ray diffraction method which is said here, and which used CuK alpha rays, and you may mainly have a crystalline diffraction line. the strongest reinforcement is 500 or less times of the diffraction line intensity of the top-most vertices of the broadcloth dispersion band looked at by 20 degrees or more 40 degrees or less with 2theta value among the crystalline diffraction lines preferably looked at by 40 degrees or more 70 degrees or less with 2theta value -- desirable -- further -- desirable -- 100 or less times -- it is -- especially -- desirable -- 5 or less times -- it is -- most -- desirable -- It is not having a crystalline diffraction line.

[0009] As for the negative-electrode material used by this invention, being expressed with the following general formula (1) is desirable. M1M2pM4qM6r General formula (1)

Among a formula, as being chosen out of Si, germanium, Sn, Pb, P, B, aluminum, and Sb in difference, M1 and M2 are kinds as it is few, they are Si, germanium, Sn, P, B, and aluminum preferably, and are Si, Sn, P, B, and aluminum especially preferably. As being chosen out of Mg, calcium, Sr, and Ba, M4 is a kind as it is few, it is Mg and calcium preferably, and is Mg especially preferably. As being chosen out of O, S, and Te, M6 is a kind as it is few, it is O and S preferably, and is O especially preferably. p and q are 0.001-10 respectively, are 0.01-5 preferably, and are 0.01-2 especially preferably. r is 1.00-50, is 1.00-26 preferably, and is 1.02-6 especially preferably. Especially the valence of M1 and M2 may not be limited, and may be an independent valence, or may be the mixture of each valence. Moreover, M2 and M4 can change continuously the ratio of M1, M2, and M4 in the range of the 0.001-10-mol equivalent to M1, and the amount (it sets to a general formula (1) and is the value of r) of M6 also changes continuously according to it.

[0010] Also in the compound mentioned above, in this invention, the case where M1 is Sn is desirable, and is expressed with a general formula (2).

SnM3pM5qM7r General formula (2)

Among a formula, as being chosen out of Si, germanium, Pb, P, B, and aluminum, M3 is a kind as it is few, it is Si, germanium, P, B, and aluminum preferably, and is Si, P, B, and aluminum especially preferably. As being chosen out of Mg, calcium, Sr, and Ba, M5 is a kind as it is few, it is Mg and calcium preferably, and is Mg especially preferably. As being chosen out of O and S, M7 is a kind as it is few, and it is O preferably. p and q are 0.001-10 respectively, are 0.01-5 preferably, are 0.01-1.5 still more preferably, and are 0.7-1.5 especially preferably. r is 1.00-50, is 1.00-26 preferably, and is 1.02-6 especially preferably.

[0011] Although the example of the negative-electrode material of this invention is shown below, this invention is not limited to these. In addition, the numeric character in () is the content (% of the weight) of Sn. $\text{SnAl0.4B0.5P0.5K0.1O3.65}$ (55.8), $\text{SnAl0.4B0.5P0.5Na0.2O3.7}$ (55.4), $\text{SnAl0.4B0.3P0.5Rb0.2O3.4}$ (54.0), $\text{SnAl0.4B0.5P0.5Cs0.1O3.65}$ (53.4), $\text{SnAl0.4B0.5P0.5K0.1germanium0.05O3.85}$ (54.1), $\text{SnAl0.4B0.5P0.5K0.1Mg0.1germanium0.02O3.83}$ (54.1), $\text{SnAl0.4B0.4P0.4O3.2}$ (60.1), $\text{SnAl0.3B0.5P0.2O2.7}$ (65.4), $\text{SnAl0.3B0.5P0.2O2.7}$ (65.4), $\text{SnAl0.4B0.5P0.3Ba0.08Mg0.08O3.26}$ (56.7), $\text{SnAl0.4B0.4P0.4Ba0.08O3.28}$ (56.6), $\text{SnAl0.4B0.5P0.5O3.6}$ (57.1), $\text{SnAl0.4B0.5P0.5Mg0.1O3.7}$ (56).

[0012] $\text{SnAl0.5B0.4P0.5Mg0.1F0.2O3.65}$ (54.8), $\text{SnB0.5P0.5Li0.1Mg0.1F0.2O3.05}$ (60.8), $\text{SnB0.5P0.5K0.1Mg0.1F0.2O3.05}$ (59.8), $\text{SnB0.5P0.5K0.05Mg0.05F0.1O3.03}$ (61.5), $\text{SnB0.5P0.5K0.05Mg0.1F0.2O3.03}$ (60.5), $\text{SnAl0.4B0.5P0.5Cs0.1Mg0.1F0.2O3.65}$ (52), $\text{SnB0.5P0.5Cs0.05Mg0.05F0.1O3.03}$ (60), $\text{SnB0.5P0.5Mg0.1F0.1O3.05}$ (61.6), $\text{SnB0.5P0.5Mg0.1F0.2O3}$ (61.2), $\text{SnB0.5P0.5Mg0.1F0.06O3.07}$ (61.7), $\text{SnB0.5P0.5Mg0.1F0.14O3.03}$ (61.4), SnPBa0.08O3.58 (54.5), SnPK0.1O3.55 (56.4), $\text{SnPK0.05Mg0.05O3.58}$ (56.5), SnPCs0.1O3.55 (54), $\text{SnPBa0.08F0.08O3.54}$ (54.2), $\text{SnPK0.1Mg0.1F0.2O3.55}$ (54.8), $\text{SnPK0.05Mg0.05F0.1O3.53}$ (56.2), $\text{SnPCs0.1Mg0.1F0.2O3.55}$ (52.5), $\text{SnPCs0.05Mg0.05F0.1O3.53}$ (55).

[0013] $\text{Sn1.1aluminum0.4B0.2P0.6Ba0.08F0.08O3.54}$ (56.5), $\text{Sn1.1aluminum0.4B0.2P0.6Li0.1K0.1Ba0.1F0.1O3.65}$ (54.3), $\text{Sn1.1aluminum0.4B0.4P0.4Ba0.08O3.34}$ (58.7), $\text{Sn1.1aluminum0.4PCs0.05O4.23}$ (52.9), $\text{Sn1.1aluminum0.4PK0.05O4.23}$ (54), $\text{Sn1.2aluminum0.5B0.3P0.4Cs0.2O3.5}$ (56), $\text{Sn1.2aluminum0.4B0.2P0.6Ba0.08O3.68}$ (58.4), $\text{Sn1.2aluminum0.4B0.2P0.6Ba0.08F0.08O3.64}$ (58.2), $\text{Sn1.2aluminum0.4B0.2P0.6Mg0.04Ba0.04O3.68}$ (59.5),

Sn1.2aluminum0.4B0.3P0.5Ba 0.08O3.58 (59.3), Sn1.3aluminum0.3B0.3P0.4Na 0.2O3.3 (65.5), Sn1.3aluminum0.2B0.4P0.4calcium 0.2O3.4 (64.6), Sn1.3aluminum0.4B0.4P0.4Ba 0.2O3.6 (57.8), Sn1.4aluminum0.4PK 0.2O4.6 (57.4), Sn1.4aluminum0.2Ba0.1PK 0.2O4.45 (56.3), Sn1.4aluminum0.2Ba0.2PK 0.2O4.6 (53.4), Sn1.4aluminum0.4PK 0.3O4.65 (56.5), Sn1.5aluminum0.2PK 0.2O4.4 (60.8), Sn1.5aluminum0.4PK 0.1O4.65 (59.7), Sn1.5aluminum0.4PCs 0.05O4.63 (59.2), Sn1.5aluminum0.4PCs0.05Mg0.1F0.2O4.63 (58).

[0014] SnSi0.5aluminum0.1B0.2P0.1calcium 0.4O3.1 (57.5), SnSi0.4aluminum 0.2B0.4O2.7 (64.9), SnSi0.5aluminum0.2B0.1P0.1Mg 0.1O2.8 (62.6), SnSi0.6aluminum 0.2B0.2O2.8 (63.2), SnSi0.5aluminum0.3B0.4P0.2O3.55(57), SnSi0.5aluminum0.3B0.4P0.5O4.30 (51.7), SnSi0.6aluminum0.1B0.1P0.3O3.25 (59.2), SnSi0.6aluminum0.1B0.1P0.1Ba 0.2O2.95 (54.7), SnSi0.6aluminum0.1B0.1P0.1calcium 0.2O2.95 (60), [0015] SnSi0.6aluminum0.4B0.2Mg 0.1O3.2 (58.7), SnSi0.6aluminum0.1B0.3P0.1O3.05 (61.4), SnSi0.6aluminum0.2Mg 0.2O2.7 (62.8), SnSi0.6aluminum0.2calcium 0.2O2.7 (61.8), SnSi0.6aluminum0.2P0.2O3 (60.8), SnSi0.6B0.2P0.2O3(62), SnSi0.8aluminum 0.2O2.9 (61.5), SnSi0.8aluminum0.3B0.2P0.2O3.85(54), SnSi 0.8B0.2O2.9 (62.6), SnSi0.8Ba 0.2O2.8 (55.6), SnSi0.8Mg 0.2O2.8 (62.2), SnSi0.8calcium 0.2O2.8 (61.2), SnSi0.8P0.2O3.1 (60.3). [0016] Sn0.9Mn0.3B0.4P0.4calcium0.1Rb 0.1O2.95 (53.5), Sn0.9Fe0.3B0.4P0.4calcium0.1Rb 0.1O2.95 (53.4), Sn0.8Pb0.2calcium0.1P0.9O3.35 (42.8), Sn0.3germanium0.7Ba0.1P0.9O3.35 (19.6), Sn0.9Mn0.1Mg0.1P0.9O3.35 (54.4), Sn0.2Mn0.8Mg0.1P0.9O3.35 (15.7), Sn0.7Pb0.3calcium0.1P0.9O3.35 (36) Sn0.2germanium0.8Ba0.1P0.9O3.35 (13.4). What was made to decrease the quantity of and increase the quantity of Sn and O of these above-mentioned compounds by this mole ratio furthermore, and adjusted the content of Sn in 5 - 70% of the weight of the range can be used preferably.

[0017] The chemical formula of the compound which baking was carried out [above-mentioned] and obtained is computable from the weight difference of the fine particles before and behind baking as inductively-coupled-plasma (ICP) emission spectrochemical analysis and a brief method as a measuring method.

[0018] 50-700-mol% per negative-electrode material of the amount of light metal insertion to the negative-electrode material of this invention is good until it approximates it to the deposition potential of the light metal, but although it is desirable, it is especially desirable, for example. [100-600-mol% of] Many the burst sizes are so desirable that there are to the amount of insertion. The insertion method of a light metal has electrochemical and the desirable chemical and thermal method. The method of inserting electrochemically the light metal contained in positive active material and the method of an electrochemical process of inserting in a direct electrochemistry target from a light metal or its alloy are desirable. The chemical method has mixing with a light metal, contact or an organic metal, for example, butyl lithium etc., and the method of making it react. An electrochemical process and the chemical method are desirable. This especially light metal has a lithium or a desirable lithium ion.

[0019] In this invention, by using the compound shown by the general formula (1) as shown above, and (2) mainly as a negative-electrode material, and the charge-and-discharge cycle property was more excellent, safety is high at high discharge voltage and high capacity, and the nonaqueous rechargeable battery excellent in the high current characteristic can be obtained. In this invention, the outstanding effect's especially being acquired is using the compound with which Sn's is contained and the valence of Sn exists with divalent as a negative-electrode material. It can ask for the valence of Sn by chemical titration actuation. For example, it can analyze by the method of a publication to 165 pages of Physicsand Chemistry of Glasses Vol.8 No.4 (1967). Moreover, it is also possible to determine from the Knight shift by solid-state nuclear-magnetic-resonance (NMR) measurement of Sn. For example, it sets to broad measurement and Metal Sn (Sn of 0 **) is Sn (CH3)4. To receiving and a peak appearing in a low magnetic field extremely with near 7000 ppm, in SnO (= divalent), it appears near 100 ppm, and appears near -600 ppm in SnO2 (= tetravalence). Thus, since a Knight shift is greatly dependent on the valence of Sn which is a central metal when it has the same ligand, the decision of a valence is attained in the peak location required in 119 Sn-NMR measurement.

[0020] Various compounds can be included in the negative-electrode material of this invention. For example, 1 group element (Li, Na, K, Rb, Cs), and transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, a lanthanoids system metal, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg) and a periodic-table 17 group element (F, Cl) can be included. Moreover, the dopant of the various compounds (for example, compound of Sb, In, and Nb) which raise electronic conduction nature may also be included. 0-20-mol% of the amount of the compound to add is desirable.

[0021] the synthesis method of the multiple oxide which makes a subject the oxide shown by the general formula (1) in this invention, and (2) -- the calcinating method and a solution method -- any method is employable. For example, what is necessary is to mix M1 compound, M2 compound, and M4 compound (for Si, germanium, Sn, Pb, P, B, aluminum, Sb, and M4 to be Mg, calcium, Sr, and Ba in difference for M1 and M2), and just to make it calcinate, when the calcinating method is explained to details. As an Sn compound, for example, SnO, SnO2, Sn 2O3, Sn3O4, Sn7O13andH2O, Sn 8O15, the first tin of hydroxylation, the second tin of oxy-hydroxylation, stannous acid, tin, the first tin of phosphoric acid, alt.stannic acid, metastannic acid, Para stannic acid, tin, the second tin of fluoridation, stannous chloride, a stannic chloride, the first tin of a pyrophosphoric acid, Lynn-ized tin, the first tin of sulfuration, a tin bisulfide, etc. can be mentioned. As an Si compound, hydro silane compounds, such as alkoxysilane compounds, such as organosilicon compounds, such as SiO2, SiO, a tetramethylsilane, and a tetraethyl silane, a tetramethoxy silane, and a tetra-ethoxy silane, and a TORIKURORO hydro silane, can be mentioned. As a germanium compound, alkoxy germanium compounds, such as GeO2, GeO, a germanium tetra-methoxide, and germanium tetra-ethoxide, etc. can be mentioned. As a Pb compound, PbO2, PbO, Pb 2O3, Pb3O4, a lead nitrate, lead carbonate, lead formate, lead acetate, a lead tetraacetate, tartaric-acid lead, lead JIETOKISHIDO, lead JI (isopropoxide), etc. can be mentioned. As a P compound, a phosphorus pentaoxide, phosphorus oxychloride, a phosphorus pentachloride, a phosphorus trichloride, phosphorus tribromide, a trimethyl phosphoric acid, a triethyl phosphoric acid, a TORIPURO pill phosphoric acid, the first tin of a pyrophosphoric acid, phosphoric-acid boron, etc. can be mentioned. As a B compound, for example, 32 boron oxide, boron trichloride, boron tribromide, boron carbide, a way acid, way acid TORIMECHIRU, way acid triethyl, tripropyl borate, way acid tributyl, boron phosphide, phosphoric-acid boron, etc. can be mentioned. As an aluminum compound, an aluminum oxide (alpha-alumina, beta-alumina), an aluminum silicate, aluminum tree iso-propoxide, tellurous-acid aluminum, an aluminum chloride, HOU-ized aluminum, aluminium phosphide, aluminium phosphate, lactic-acid aluminum, way acid aluminum, aluminum sulfate, an aluminum sulfate, HOU-ized aluminum, etc. can be mentioned. As a Sb compound, for example, 3 oxidation 2 antimony, triphenyl antimony, etc. can be mentioned.

[0022] As Mg, calcium, Sr, and a Ba compound, each oxidation salt, a hydroxylation salt, a carbonate, phosphate, a sulfate, a nitrate, an aluminium compound, etc. can be mentioned.

[0023] As baking conditions, it is 6 degrees C or more 2000 degrees C or less that it is 4-degree-C [or more]/m programming rate of 2000 degrees C or less as a programming rate desirable still more preferably. Are 10 degrees C or more 2000 degrees C or less, and it is

especially preferably desirable as a burning temperature that it is [250 degrees-C or more] 1500 degrees C or less. It is 350 degrees C or more 1500 degrees C or less still more preferably, and is 500 degrees C or more 1500 degrees C or less especially preferably. And it is desirable that it is 100 or less hours as firing time for 0.01 hours or more. It is 70 or less hours still more preferably for 0.5 hours or more, and is 20 or less hours especially preferably for 1 hour or more. And as a temperature fall speed, it is 4 degrees C or more 107 degrees C or less that it is [2 degrees-C / or more //m] 107 degrees C or less desirable still more preferably, and it is 6 degrees C or more 107 degrees C or less especially preferably, and is 10 degrees C or more 107 degrees C or less especially preferably. The programming rate in this invention is the mean velocity of a temperature rise until it reaches "80% of burning temperature (degree-C display)" from "50% of burning temperature (degree-C display)", and the temperature fall speed in this invention is the mean velocity of a temperature reduction until it reaches "50% of burning temperature (degree-C display)" from "80% of burning temperature (degree-C display)." You may cool all over a firing furnace and a temperature fall is taken out outside a firing furnace again, for example, may be supplied underwater and may be cooled. moreover, gun given in 217 pages (Gihodo Shuppan 1987) of ceramic processing -- law -Hammer-Anvil -- law -slap -- law -- the - gas atomizing method, the plasma-spraying method, a centrifugal quenching method, and melt drag -- super-quenching methods, such as law, can also be used. Moreover, you may cool using the single roller method given in 172 pages (Maruzen 1991) of new glass handbooks, and a congruence roller. In the case of the material fused during baking, a baking object may be taken out continuously, supplying a raw material during baking. It is desirable to stir melt in the case of the material fused during baking.

[0024] Oxygen content is an ambient atmosphere below 5 volume % preferably, and a baking gas ambient atmosphere is an inert gas ambient atmosphere still more preferably. Nitrogen, an argon, helium, a krypton, a xenon, etc. are mentioned as inert gas.

[0025] The average grain size of the compound shown by the general formula (1) used by this invention and (2) has desirable 0.1-60 micrometers, especially its 1.0-30 micrometers are desirable, and its 2.0-20 micrometers are still more desirable. In order to make it a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planet ball mill, a revolution air-current mold jet mill, a screen, etc. are used. At the time of grinding, wet grinding which made organic solvents, such as water or a methanol, live together can also be performed if needed. It is desirable to perform a classification, in order to consider as a desired particle size. As the classification method, there is especially no limitation and it can use a screen, a pneumatic elutriation machine, etc. if needed. A classification can use dry type and wet. It is desirable to apply the water distribution object with which a negative-electrode sheet contains a negative-electrode material, a binder, and an electric conduction agent on copper foil.

[0026] The positive electrode of this invention comes to paint more than two-layer [that contains reversibly the positive-electrode material in which occlusion emission is possible for a lithium] on a charge collector. In the gestalt which comes to paint the layer containing a positive-electrode material on both sides of a charge collector, the spreading layer on one side is more than two-layer at least, and a double-sided spreading layer is more than two-layer preferably. These spreading layers are formed mainly from a positive-electrode material, a binder, and an electrical conducting material, respectively. The especially furthest layer from a charge collector contains an insulating solid particulate. The content of a positive-electrode material is the rate that a positive-electrode material occupies in the formed element of the painted positive-electrode layer, and it expresses with weight %. this invention -- setting -- a positive-electrode layer -- from the layer more than two-layer -- becoming -- the mixture of the furthest layer from a charge collector -- the contents of an inner positive-electrode material are 10 % of the weight or more and 60 % of the weight or less, and it is desirable that the content of the positive-electrode material of other layers carries out to 70 % of the weight or more and 98% of the weight or less on an average. Here, the furthest layer from a charge collector puts the maximum upper layer. furthermore, a positive-electrode layer -- from the layer more than two-layer -- becoming -- the mixture of the furthest layer from a charge collector -- the contents of an inner positive-electrode material are 10 % of the weight or more and 50 % of the weight or less, and it is more desirable that the contents of the positive-electrode material of other layers are 80 % of the weight or more and 98 % of the weight or less on an average. Especially the insulating solid particulate preferably contained in the maximum upper layer is an oxide, and a titanium dioxide most preferably. It is more desirable to mix and compound as a desirable RIUMU content transition-metals oxide positive-electrode material, so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from Ti, V, Cr, Mn, Fe, Co, nickel, Mo, and W with transition metals here) may be set to 0.3-2.2 rather than being used by this invention. It is desirable to mix and compound so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from V, Cr, Mn, Fe, Co, and nickel with transition metals here) may be set to 0.3-2.2 as an especially desirable lithium content transition-metals oxide positive-electrode material used by this invention. It is desirable that the especially desirable lithium content transition-metals oxide positive-electrode materials used by this invention are Li_xQO_y (Q is mainly the transition metals with which a kind contains Co, Mn, nickel, V, and Fe at least here), $x=0.02-2.2$, and $y=1.4-3$. As Q, aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. may be mixed in addition to transition metals. 0-30-mol% of the amount of mixing is desirable to transition metals.

[0027] As a desirable lithium content metallic-oxide positive-electrode material, to the pan used by this invention Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{CoaNi1-aO}_2$, and $\text{Li}_x\text{CobV1-bO}_2$, $\text{Li}_x\text{CobFe1-bO}_2$, $\text{Li}_x\text{Mn2O}_4$, $\text{Li}_x\text{MncCo2-cO}_4$, $\text{Li}_x\text{MncNi2-cO}_4$, $\text{Li}_x\text{MncV2-cO}_4$, and $\text{Li}_x\text{MncFe2-cO}_4$ (here -- $x=0.02-2.2$, $a=0.1$ to 0.9 , and $b=0.8$ to 0.98 --) $c=1.6-1.96$ and $z=2.01-2.3$ are raised. As most desirable lithium content transition-metals oxide positive-electrode material used by this invention, Li_xCoO_2 , Li_xNiO_2 , Li_xMnO_2 , $\text{Li}_x\text{CoaNi1-aO}_2$, $\text{Li}_x\text{Mn2O}_4$, and $\text{Li}_x\text{CobV1-bO}_2$ (it is $x=0.02-2.2$, $a=0.1$ to 0.9 , $b=0.9$ to 0.98 , and $z=2.01-2.3$ here) are raised. Here, the x above-mentioned values are values before charge-and-discharge initiation, and are fluctuated by charge and discharge.

[0028] positive and the negative electrode used for the nonaqueous rechargeable battery of this invention -- a positive electrode -- a mixture or a negative electrode -- a mixture can be fabricated and made on a charge collector at painting or a pellet type. a positive electrode or a negative electrode -- everything but a positive-electrode material or a negative-electrode material can be looked like [a mixture], respectively, and can contain an electric conduction agent, a binder, a dispersant, a filler, an ion electric conduction agent, a pressure enhancement agent and insulation, conductivity, and the solid-state particle and the various additives of half-conductivity in it, respectively.

[0029] The binders in the positive electrode which can be used by this invention, and a negative electrode are polyacrylic acid, a carboxymethyl cellulose, polytetrafluoroethylene, polyvinylidene fluoride, polyvinyl alcohol, starch, diacetyl cellulose, hydroxypropylcellulose, polyvinyl chloride, a polyvinyl pyrrolidone, polyethylene, polypropylene, SBR, EPDM, sulfonation EPDM, a fluororubber, polybutadiene, and polyethylene oxide, and polyacrylic acid, a carboxymethyl cellulose, polytetrafluoroethylene, and its polyvinylidene fluoride are especially desirable.

[0030] An insulating individual particle can be contained in the negative electrode of this invention, and a positive electrode. The particle

of the desirable organic substance is the powdery part of the latex over which the bridge was constructed, or a fluoro-resin, and what is 300 degrees C or less, and does not decompose, or does not form a coat is desirable. The impalpable powder of Teflon is more desirable. As an inorganic substance particle, a metal, the carbide of a nonmetallic element, silicide, a nitride, a sulfide, and an oxide can be mentioned. In carbide, silicide, and a nitride, SiC, aluminum nitride (AlN), and BN and BP of insulation are chemically [highly and] stable, and are desirable, and especially SiC using especially BeO, Be, and BN as a sintering assistant is desirable. In chalcogenide, an oxide is desirable. As these oxides, aluminum 2O₃, As₄O₆, B₂S₃, BaO, BeO, and CaO, Li₂O, K₂O, Na₂O, In₂O₃, MgO and Sb₂O₅, and SiO₂, TiO₂, SrO and ZrO₂ are raised. In these, especially aluminum 2O₃, BaO, BeO and CaO, K₂O, Na₂O, and MgO, SiO₂, TiO₂, SrO and ZrO₂ are desirable. The insulating solid particulate contained in the maximum upper layer of a positive electrode has the most desirable titanium dioxide. These oxides may be independent or may be multiple oxides. As a compound desirable as a multiple oxide, a mullite (3aluminum2O₃ and 2SiO₂), a steatite (MgO-SiO₂), forsterite (2 MgO-SiO₂), cordierite (2MgO, 2aluminum2O₃, and 5SiO₂), etc. can be mentioned. 20 micrometers or less 0.1 micrometers or more are especially used preferably by methods, such as control of a generation condition, and grinding, by making these inorganic compound particles into a particle (0.2 micrometers or more and 15 micrometers or less).

[0031] As the quality of the material, it is aluminum, stainless steel, nickel, titanium, or these alloys at a positive electrode, the base materials, i.e., the charge collector, of the positive electrode which can be used by this invention, and a negative electrode, they are copper, stainless steel, nickel, titanium, or these alloys at a negative electrode, and are a foil, an expanded metal, a punching metal, and a wire gauze as a gestalt. Especially, to a positive electrode, copper foil is [aluminium foil and a negative electrode] desirable. The separator which can be used by this invention has large ion transmittance, and it has a predetermined mechanical strength, and that what is necessary is just an insulating thin film, as the quality of the material, olefin system polymer, fluorine system polymer, cellulose system polymer, polyimide, nylon, a glass fiber, and an alumina fiber are used, and a nonwoven fabric, textile fabrics, and a microporous film are used as a gestalt. Especially, as the quality of the material, the mixture of polypropylene, polyethylene, polypropylene, the mixture of polyethylene and polypropylene, and Teflon and the mixture of polyethylene and Teflon are desirable, and what is a microporous film as a gestalt is desirable. Especially, the microporous film whose aperture is 0.01-1 micrometer and whose thickness is 5-50 micrometers is desirable.

[0032] The electrolytic solution which can be used by this invention as an organic solvent Propylene carbonate, Ethylene carbonate, butylene carbonate, dimethyl carbonate, Diethyl carbonate, 1, 2-dimethoxyethane, gamma-butyrolactone, A tetrahydrofuran, 2-methyl tetrahydrofuran, dimethyl SUFOKISHIDO, Dioxolane, 1, 3-dioxolane, a formamide, dimethylformamide, Nitromethane, an acetonitrile, methyl formate, methyl acetate, methyl propionate, Phosphoric acid triester, trimethoxy methane, a dioxolane derivative, a sulfolane, As 3-methyl-2-oxazolidinone, a propylene carbonate derivative, a tetrahydro derivative, diethylether, 1, the thing that mixed at least one or more sorts of 3-propane ape ton, and an electrolyte LiClO₄, LiBF₄, LiPF₆, LiCF₃SO₃, LiCF₃CO₂, LiAsF₆ and LiSbF₆, LiB₁₀Cl₁₀, a low-grade aliphatic-carboxylic-acid lithium, What dissolved one or more sorts of salts of LiAlCl₄, LiCl, LiBr, LiI, a chloro borane lithium, and 4 phenyl lithium borate is desirable. They are LiCF₃SO₃, LiClO₄ and LiBF₄ and/, or LiPF₆ especially to a mixed solvent with propylene carbonate or ethylene carbonate, 1 and 2-dimethoxyethane and/, or diethyl carbonate. What was dissolved is desirable and it is desirable that ethylene carbonate and LiPF₆ are included especially at least.

[0033] The configuration of a cell is applicable to both a carbon button, coin a sheet a cylinder an angle, etc. In a carbon button and coin, press forming of the mixture is carried out to a pellet type, it is used for it, and on a charge collector, paint and dry it, it is dehydrated, and a mixture is pressed and is used in a sheet, an angle, and a cylinder. A cell inserts in a cell can the electrode wound with a pellet, the shape of a sheet, and a separator, connects an electrode with a can electrically, and the electrolytic solution is poured in, and it obturates and forms it. At this time, a relief valve can be used as an obturation board. Furthermore, in order to guarantee the safety of a cell, it is desirable to use a PTC element.

[0034] The closed-end cell sheathing cans which can be used by this invention are the iron steel plate which performed nickel plating as the quality of the material, a stainless steel plate (SUS304, SUS304 L, SUS304 N, SUS316, SUS316 L, SUS430, SUS444 grade), the stainless steel plate (same as the above) which performed nickel plating, aluminum or its alloy, nickel, titanium, and copper, and are perfect circle form tubed, ellipse form tubed, square tubed, and rectangle tubed as a configuration. Especially when a sheathing can serves as a negative-electrode terminal, a stainless steel plate and the iron steel plate which performed nickel plating are desirable, and when a sheathing can serves as a positive-electrode terminal, a stainless steel plate, aluminum, or its alloy is desirable.

[0035] As the quality of the material, they are olefin system polymer, fluorine system polymer, cellulose system polymer, polyimide, and a polyamide, from organic solvent-proof nature and low-water-flow part permeability, the gasket which can be used by this invention has desirable olefin system polymer, and especially its polymer of a propylene subject is desirable. Furthermore, it is desirable that it is the block copolymerization polymer of a propylene and ethylene.

[0036] The cell of this invention is covered with a sheathing material if needed. As a sheathing material, there are heat-shrinkable tubing, adhesive tape, a metal film, paper, cloth, a coating, a plastics case, etc. Moreover, the portion of sheathing discolored with heat in part at least is prepared, and you may make it the heat history in use known. The cell of this invention constructs two or more to a serial and/or juxtaposition if needed, and is contained by the cell pack. A safety circuit (circuit with the function which intercepts current if it acts as the monitor of the voltage of each cell and/or the whole group cell, temperature, the current, etc. and is required) besides safety elements, such as a positive temperature coefficient resistor, a thermal fuse, a fuse, and/or a current cutoff element, may be prepared in a cell pack. Moreover, the positive electrode of each cell and a negative-electrode terminal, the whole group cell and the temperature element child of each cell, the current element child of the whole group cell, etc. can also be prepared in a cell pack as an external terminal in addition to the positive electrode of the whole group cell, and a negative-electrode terminal. Moreover, voltage conversion circuits (DC-DC converter etc.) may be built in a cell pack. Moreover, you may fix by welding a lead board, and connection of each cell may be fixed so that it can detach and attach easily with a socket etc. Furthermore, display functions, such as cell remaining capacity, existence of charge, and a use count, may be prepared in a cell pack.

[0037] The cell of this invention is used for various devices. It is desirable to be especially used for a video movie, a pocket mold videocassette recorder with a built-in monitor, a movie camera with a built-in monitor, a compact camera, a single-lens reflex camera, a disposable camera, a disposable camera, a notebook sized personal computer, a note type word processor, an electronic notebook, a cellular phone, a cordless telephone, a mustached camber, a power tool, an electric mixer, an automobile, etc.

[0038]

[Example] Although an example is raised to below and this invention is explained in more detail, unless the main point of invention is exceeded, this invention is not limited to an example.

[0039] 6.7g [of synthetic example -1 tin protoxides], 10.3g [of pyrophosphoric-acid tin], 1.7g [of boron oxide], 0.7g [of potassium carbonate], 0.4g [of magnesium oxides], and diacid-ized germanium 1.0g was blended dryly, it put into the crucible made from an alumina, and the temperature up was carried out to 1000 degrees C by part for bottom 15-degree-C/ of an argon ambient atmosphere. After calcinating at 1200 degrees C for 12 hours, even the room temperature cost whenever [temperature fall] by part for 10-degree-C/, it took out from the firing furnace, and SnGe0.1 B0.5 P0.5 aluminum0.44Mg 0.1K0.1O3.86 was obtained. The jet mill ground this and powder with a mean particle diameter of 4.5 micrometers was obtained (compound -1-1). This is an object which has the broadcloth peak which has top-most vertices near 28 degree with 2theta value in the X-ray diffraction method which used CuK alpha rays, and the crystalline diffraction line was not looked at by 40 degrees or more 70 degrees or less with 2theta value.

[0040] The raw material of the amount of stoichiometries was mixed, calcinated and ground like the synthetic example -2, respectively, and the following compound was obtained.

SnGe0.1 B0.5 P0.5 aluminum0.44Mg 0.1K0.1O3.91 (compound 2-1)

SnSi0.5 germanium0.1 K0.1 aluminum0.2 B0.1 P0.1 Mg 0.1O2.95 (compound 2-2)

SnSi0.6 aluminum0.1 B0.1 P0.1 Ba 0.2O2.95 (compound 2-3)

SnSi0.6 aluminum0.1 B0.1 P0.1 calcium 0.2O2.95 (compound 2-4)

[0041] As a production negative-electrode material of example -1 sample -1, using the compound 1-1 compounded in the synthetic example -1, it was mixed 86% of the weight at a rate of 6 % of the weight of scale-like graphites, and 3 % of the weight of acetylene black, 4 % of the weight and 1 % of the weight of carboxymethyl celluloses were further added for the water distribution object of polyvinylidene fluoride as a binder, water was kneaded as data medium, and the negative-electrode slurry 1 was produced. 9 % of the weight of scale-like graphites and 9 % of the weight of carboxymethyl celluloses were added for aluminum2O3, TiO2, and alpha-aluminum 2O3 82% of the weight, water was kneaded as data medium, and the negative-electrode slurry 2 was made. The negative-electrode slurry 1 was made into the copper foil side on 18-micrometer copper foil, and on it, the negative-electrode slurry 2 was piled up and it applied by the extrusion method at coincidence. The coverage per one side was 71 g/m2 and 12 g/m2 in the mixture, respectively. Coincidence spreading was similarly carried out to the opposite side of copper foil. It dried at about 50 degrees C. Compression molding of the spreading negative electrode was carried out with the calender press machine, it cut to predetermined width of face and length, and the band-like negative-electrode sheet -1 was produced. The thickness of the negative-electrode sheet -1 was 98 micrometers. As a positive-electrode material, it is LiCoO2. 93% of the weight, 1 % of the weight of scale-like graphites, and 4 % of the weight of acetylene black, 1 % of the weight of polytetrafluoroethylene water distribution objects and 1 % of the weight of sodium polyacrylate were further added as a binder, water was kneaded as data medium, and the positive-electrode slurry 1 was obtained. Moreover, LiCoO2 15% of the weight, these positive-electrode slurries 1 and 2 that added 3 % of the weight of polytetrafluoroethylene water distribution objects and 1 % of the weight of sodium polyacrylate as 1 % of the weight of acetylene black and a binder 80% of the weight, kneaded water as data medium, and obtained the positive-electrode slurry 2 were applied by the method same to both sides of aluminium foil with a thickness of 20 micrometers as the above, it dried, alpha-aluminum 2O3 was pressed, and it cut. The coverage per one side was 341 g/m2 and 10 g/m2 in the mixture, respectively. The 200-micrometer band-like positive-electrode sheet -1 was produced. The above-mentioned negative-electrode sheet -1 and the positive-electrode sheet -1 are each the dew-point after carrying out spot welding of the lead board of nickel and aluminum to an edge, respectively. - Dehydration desiccation was carried out in dry air 40 degrees C or less for 200-degree-C 2 hours. Furthermore, the laminating was carried out in the order of a dried [dehydration] positive-electrode sheet (8) fine porosity polypropylene film separator (Celgard 2400), a dried [dehydration] negative-electrode sheet (9), and a separator (10), and this was wound around the curled form with the contamination machine.

[0042] It contained with the iron closed-end cylindrical cell can (11) which serves this winding object as a negative-electrode terminal and which performed nickel plating. It is LiPF6 per l. LiBF4 They are 0.9 and 0.1 mols respectively. It contained and the electrolyte with which a solvent consists of 2:2:6 capacity mixed liquor of ethylene carbonate, butylene carbonate, and dimethyl carbonate was poured into the cell can. the cell lid (12) which has a positive-electrode terminal -- a gasket (13) -- minding -- the cylindrical cell was produced in total. In addition, the positive-electrode terminal (12) connected beforehand the positive-electrode sheet (8) and the cell can (11) with the negative-electrode sheet (9) with the lead terminal. The cross section of a cylindrical cell was shown in drawing 1. In addition, (14) is a relief valve. Sample - Production of 2-5.

It is a sample like a sample -1 except having set the negative-electrode material to 2-1, 2-2, 2-3, and 2-4 respectively. - 2-5 were produced.

[0043] The positive-electrode sheet -2 as well as the positive-electrode sheet -1 was produced except having not applied the production positive-electrode slurry 2 of the example of a comparison. Example of comparison-A was produced like the sample -1 except having used the positive-electrode sheet -2 instead of the positive-electrode sheet -1.

[0044] Sample - 1-5, example of a comparison - It produces all 100 A at a time, and is 0.4 mA/cm2. With current, it charged to 4.2V and the open circuit voltage after 25-degree-C one-month conservation was measured in the state of charge. The rate from which open circuit voltage became less than [4.1V] is a sample. - They were 1.8%, 2.0%, 2.0%, 1.9%, and 1.7% respectively in 1-5. Moreover, example of a comparison - In A, it was 3.8%. Sample of this invention - Compared with example of comparison-A, it is small, a manufacture yield is high, and 1-5 had the desirable fall of open circuit voltage.

[0045] The positive-electrode sheet 3 was produced by the same method as an example except having changed alpha-aluminum 2O3 of the example-2 positive-electrode slurry 2 into TiO2. 10 was produced from the sample -6 like 5 from a sample -1 except having used the positive-electrode sheet -3. It produces 100 10 at a time from a sample -6, and is 0.4 mA/cm2. With current, it charged to 4.2V and the open circuit voltage after 25-degree-C one-month conservation was measured in the state of charge. The rate from which open circuit voltage became less than [4.1V] is a sample. - They were 1.3%, 1.0%, 1.2%, 1.1%, and 0.9% respectively in 6-10. The samples 6-10 of this invention had the small desirable fall of open circuit voltage compared with samples 1-5.

[0046] example -3 negative electrode -- a mixture -- having stuck the 120mg [per 1g of negative-electrode materials] lithium metallic foil in the shape of a strip of paper upwards, and having made it contact electrically, and a positive electrode -- the same result as a repeat was obtained for the example -1 except having made coverage of a mixture into 240 g/m2 on one side.

[0047] From the sample -1 of example -4 example -1, it produces each 10 and 100 example of comparison-A from 5 and the sample -6 of an example -2, and is 0.4 mA/cm2. With current, it charged to 4.2V and the open circuit voltage after 60-degree-C 1.5-month conservation was measured in the state of charge. 10 and example of comparison-A of the fall of open circuit voltage were 0.09V, 0.09V, 0.10V, 0.08V, 0.09V, 0.07V, 0.06V, 0.06V, 0.07V, 0.06V, and 0.15V respectively from the sample -1 by the average. Compared with example of comparison-A, the fall of open circuit voltage of 10 was small desirable from the sample -1 of this invention. Especially the samples 6-10

had the small desirable fall of open circuit voltage.

[0048] The same result as a repeat was obtained for the example -4 except having set respectively ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propionate, and ethyl propionate to capacity factor 10/10/10/20/20/20/5/5 for the solvent of the example -5 electrolytic solution.

[0049]

[Effect of the Invention] The nonaqueous rechargeable battery which gives the productivity which was excellent with the configuration which a negative-electrode layer or a positive-electrode layer consists of more than two-layer, and the positive-electrode contents of a positive-electrode binder layer differ like this invention, and contains an insulating solid particulate in the maximum upper layer, and shelf life can be obtained.

[Translation done.]